



Short communication

Electrochemical performance of cathodes prepared on current collector with different surface morphologies



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HIGHLIGHTS

- The electrochemical performance of cathodes was influenced by the surface morphology of the current collector.
- The surface roughening of the current collector improved the rate capacity of the cathode electrode.
- The surface roughening of the current collector results in the lowering of the interfacial impedances.

ARTICLE INFO

Article history:

Received 29 October 2012

Received in revised form

21 December 2012

Accepted 8 February 2013

Available online 16 February 2013

Keywords:

Cathode

Current collector

Potential profile

Complex impedance

ABSTRACT

$\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode electrodes were prepared onto Al current collectors with different surface morphologies through usual doctor blade technique. Their electrochemical performances, especially at high current rate, were influenced by the surface morphology of the current collector. These implied the less polarization for the electrode prepared on the surface roughened current collector. In addition, the AC complex impedance analysis exhibited that the interface resistance between the film electrode and the current collector as well as the interface resistance between the electrode and the electrolyte was reduced in the case of the surface-roughened current collector, but that the Ohmic resistance was enlarged.

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1. Introduction

Rechargeable lithium batteries are one of the key devices for various portable electronics, such as cellular phones and laptop computers. Recently, the utilization of renewable energy such as solar and wind powers requires a significant improvement, that is, long cycling life for the electrical energy devices. Additionally, with respect to performance and capacity, the rechargeable lithium batteries have become one of the best options for electrically driven vehicles such as electric vehicle (EV), hybrid-EV (HEV) and plug-in HEV (p-HEV). In the battery system, the cathode material strongly influences the electrochemical performance: capacity, potential, cycle and thermal stability and so on. Layered rock-salt compound

LiCoO_2 is one of the developed cathode materials which has been commercially used because of good performance, stability and easy of production, despite both high cost and toxicity. Therefore, many studies have been focused on several lithium transition metal oxides which are alternative intercalation compounds with large energy density, high output power and environmental compatibility.

On the other hand, it is well known that the electrodes are composite films. The electrochemical-active material powders were mixed with conducting additive (acetylene black) and organic binder (PVdF), and they were suspended in NMP solvent, coated onto current collector by doctor blade method and roll-compacted for densification. Considering these fabrication processes, the electrode performances depend not only on the kind of the electrochemical-active material and their particle size and morphology, but also their dispersion state, the volume fraction of the components and etc. [1–4]. Both large loading of the electrochemical active material and thickening of the electrode are

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aimed for the battery application with high energy density, while small loading and thinning of the electrode are suitable for the battery having high power capability. Consequently, there exist a trade-off relationship between high energy density and high power performances.

Apart from these facts, the surface morphology of the current collector may play an important role on the electrode performance. For example, three-dimensional porous template has been studied in order to attain high rate capability of the electrode [5–8]. During the electrochemical cycling of the electrode, the active materials are particularly subjected to inelastic deformation, due to a finite volumetric variation with delithiation/lithiation reactions. These deformations bring about the isolation of the electrochemical-active material particles from the conducting network, due to the crack formation within the composite electrode and the particle fracturing [9,10], and it is possible to peel the film electrode from the current collector, which also results in the conducting network breakdown. If the conducting path is lost, both the cycling performance and the rate capability of the cathode can be degraded.

In this work, the coating film electrodes are fabricated with $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ particles as the electrochemical active material onto Al current collectors with different surface morphologies and the experimental results about the cathode performance are presented. Their rate and cycling capabilities are examined with help of the complex impedance spectral studies. Consequently, the effect of the interface between current collector and cathode film on the electrochemical performance of the cathode is also briefly discussed.

2. Experimental

Cathode active material $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$, utilized in this study, was supplied from Tanaka Chemical Corporation. They were aggregated secondary particles of the primary particles, and the aggregated size was approximately 10 μm . They were mechanically dispersed together with acetylene black (conducting additive) in NMP solution containing PVdF binder, where the weight ratio of active material/acetylene black/PVdF was adjusted to 86/7/7. Then, the cathode films were prepared through doctor blade technique on two different Al current collectors. One of them was a normal Al sheet without surface modification. The other was pre-treated with chemical process, and there were many pores, the size of which ranged from sub-micron to micron-meter. Their SEM microphotographs were shown in Fig. 1. Both cathode films were prepared under well-controlled conditions, so that the average thickness was approximately 40 μm and active material loading was approximately 10 mg cm^{-2} .

The Li-coin cells were fabricated in an Ar-filled glove box with the cathode (the diameter of 16 mm), Li metal as counter electrode

and 1.0 M $\text{LiPF}_6/\text{EC-DMC}$ electrolyte solution. The galvano-static charge–discharge cycling was carried out at a constant charging rate of 0.1 C and various discharging current rates ranging from C/10 to 20 C, where the upper and lower limits of the charging and discharging voltage were adjusted to 4.5 and 2.5 V, respectively, and the discharging capacities and profiles were evaluated as a function of the discharging current. In the electrochemical impedance measurement, the other cells were constructed with the cathode (the diameter of 16 mm), Li metal as counter electrode, Li metal reference electrode and 1.0 M $\text{LiPF}_6/\text{EC-DMC}$ electrolyte solution. They were subjected to the galvano-static cycling at the constant current rate of 0.1 C, and after every charging, the complex impedance was measured at the frequency range from 10 mHz to 100 kHz.

3. Results and discussion

Powder X-ray diffraction of the cathode material $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ used in this study was shown in Fig. 2. They are $\alpha\text{-NaFeO}_2$ type hexagonal compounds with the lattice parameters of $a = 2.864 \text{ \AA}$ and $c = 14.243 \text{ \AA}$. They are secondary particles with near-spherical shape and diameter of 5–20 μm , and composed of fine primary particles. Fig. 3 shows the potential profiles of the electrochemical cycling at low current rate (0.1 C). It was found that both the potential profile and the capacities are almost independent of the surface morphology of the current collector. On the charging process, the voltage rapidly increases up to approximately 3.6 V, shows a gradual rising and then reaches the upper limit voltage. The voltage gradually decreases to about 3.6 V with the progress of the discharging, then rapidly decreases and attains the lower limit voltage. The initial charge and discharge capacity was 205 mAh g^{-1} and 178 mAh g^{-1} , respectively. These are typical feature of $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ layered rock-salt compound.

The discharge profiles are shown in Fig. 4, where the charging current was constant of 0.1 C and the discharge reaction was also carried out in the constant current mode, where the current was subjected to step-by-step increase in the range from 0.1 C to 10 C. The discharge profiles shifted toward lower voltage, as the discharge current increased. Then the period required to reach the lower limit voltage was reduced, that is, the discharge capacity also decreased. This is attributed to the kinetic limitation; the polarization becomes larger with the operating current. The phenomena were observed, irrespective to the current collector modification. But the variation degrees of the potential profiles as a function of the discharge current rate were slightly different: it was clear that the discharge potential profile at high current rate depends on the surface morphology of the current collector. To clarify the differences, the average potential of the discharging reaction was plotted as a function of the discharge current rate in Fig. 5(a), and the

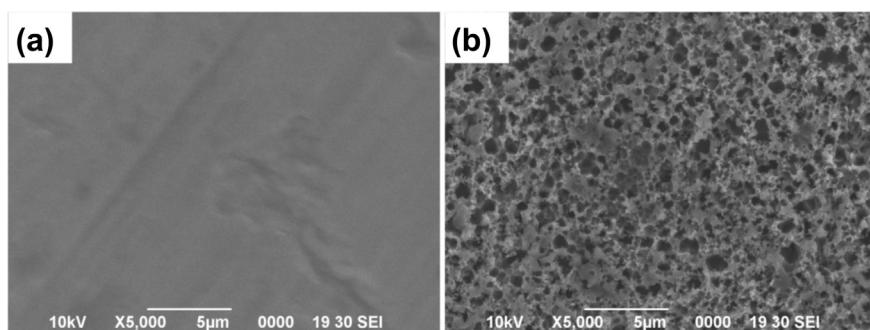


Fig. 1. SEM photographs of the Al current collectors: (a) the normal current collector with smooth surface and (b) the surface-modified current collector with rough surface.

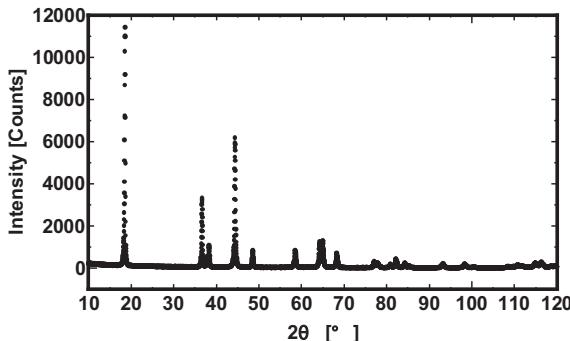


Fig. 2. Powder X-ray diffraction pattern of $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode material.

relationship between the discharge capacity and the discharge current rate was presented in Fig. 5(b). It was clearly found that the cathode prepared on the surface-modified current collector has higher average discharging potential than that of the normal current collector and that the potential difference becomes remarkable with an increase in the current rate. In addition, it was shown that the cathode prepared onto the surface-modified current collector exhibits higher discharge capacity than that on the normal current collector in the case of the discharge current rate greater than 1 C, below which both of them have almost the same capacities. These results imply that if the cathode film is prepared on the surface modified current collector, the material utilization at high current rate is improved with the lowering of the polarization. In other word, the surface morphology of the current collector has an important role on the electrochemical reaction of the cathode material under large current rates.

In order to evaluate the influence of the surface morphology of the current collector on the capacity fading during the electrochemical charge/discharge cycling, the constant current charge/discharge cycling at the current rate of 0.1 C was carried out using the three-electrode cell, and the complex impedance spectra were taken at every charging end point after rest time of 30 min. The charge–discharge profiles are shown in Fig. 6. Both the initial discharge capacity and the Coulomb efficiency in the first cycle were almost independent of the current collector, and the values were 178 mAh g^{-1} and 86%. The discharging capacity only slightly decreased with an increase in the cycling numbers: the capacity retention after 30th cycles was 91 and 94% for the cathode prepared on the flat surface current collector and the surface-roughened

current collector, respectively. During the cycling, the lowering of the average discharge potential was severe in the whole range for the former but found at the late stage for the latter. It gave a difference of the cycle fading of the capacity. That is, the capacity retention was slightly improved with use of the surface-modified current collector.

Fig. 7 shows some typical complex impedance trace in the Nyquist form and their variations on the electrochemical cycling. The typical impedance trace consisted of a depressed semicircle and a tangential line, and these features are common to the two different current collectors. The differences between these two cathodes are as follows. For the cathode prepared on the surface-roughened current collector, the impedance trace almost remains unchanged with the progress of the electrochemical cycling. On the other hand, the impedance trace gradually changes with the electrochemical cycling, and in particular, the diameter of the depressed semicircle increases with the cycling. And the other different point is that the high-frequency intercept of the impedance for the cathode prepared on the surface-roughened current collector has a larger value than that prepared on the normal current collector. In order to clarify these contributions, the complex impedance spectra were numerically evaluated with an equivalent circuit model, which was proposed by Dr. Schmidt [11]. Following their results, it is possible that the depressed semicircle is decomposed to two semicircles and they are attributed to a charge transfer at the interface between cathode film and current collector and the other charge transfer at the interface between cathode film and electrolyte solution. The former is attributed to the electronic transfer and the latter is related to the Li^+ ionic transfer. Generally speaking, the electronic transfer is faster than the ionic transfer and then the electronic transfer impedance has a smaller time constant than the ionic one does. In other word, the high-frequency response in the depressed semicircle is attributed to the electronic transfer at the electrode/current collector interface, while the low-frequency component in the depressed semicircle is attributed to the ionic charge transfer at the interface between the electrode and the electrolyte solution. Considering these facts, the depressed semicircle in the complex impedance spectra was numerically decomposed to these two components. There, the high-frequency intercept is related to the Ohmic resistance, which contains the resistances of the organic electrolyte, the current collector and etc. The Ohmic resistance was almost constant and did not vary with the electrochemical cycling, and its value (approximately 9Ω) of the cathode prepared on the surface-modified current collector was always larger than that on the normal current collector (approximately 6Ω).

The variations of the charge transfer resistances with the cycling are shown in Fig. 8. The charge transfer resistance at the electrode/current collector interface for the cathode coated onto the normal current collector increased with the cycling number. It is likely that the resistance increment comes from the weak bonding and peeling of the electrode, which is induced by the deformation of the cathode particles on the delithiation/lithiation reaction. But for the cathode prepared on the surface-modified current collector, the charge transfer resistance was almost constant during the electrochemical cycling. It can imply that the bonding of the cathode film and the surface-modified current collector is strong enough to prevail against the strain caused by the particle deformation. The strong binding between the cathode film and the surface-modified current collector may be due to the anchoring effect of the surface roughening. Next, let us look into the charge transfer resistance at the electrode/electrolyte solution interface. It was seen that, on the electrochemical cycling, the charge transfer resistance at the electrode/electrolyte solution interface has the same trends as that of at the electrode/current collector interface. For the cathode prepared

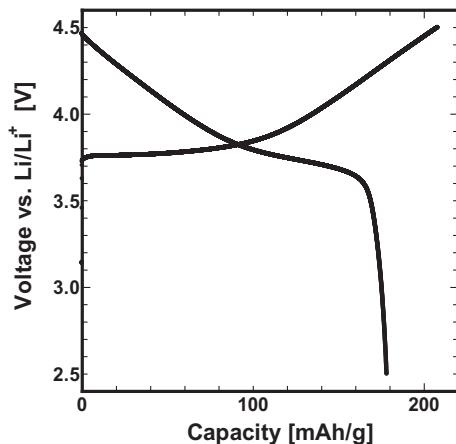


Fig. 3. Initial charging/discharging curves of the cathode film at the constant current rate of 0.1 C.

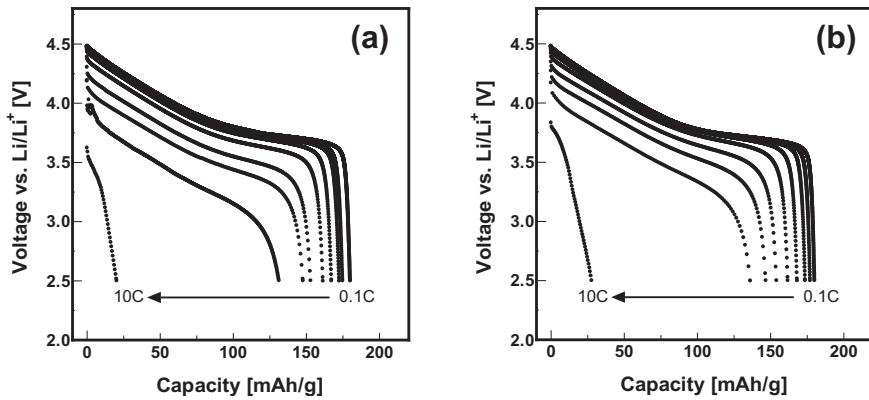


Fig. 4. Discharge profiles of the cathode films prepared on the normal current collector (a) and the surface-modified current collector (b). The discharge current was adjusted at 0.1 C, 0.2 C, 0.3 C, 0.5 C, 1 C, 2 C, 3 C, 5 C and 10 C.

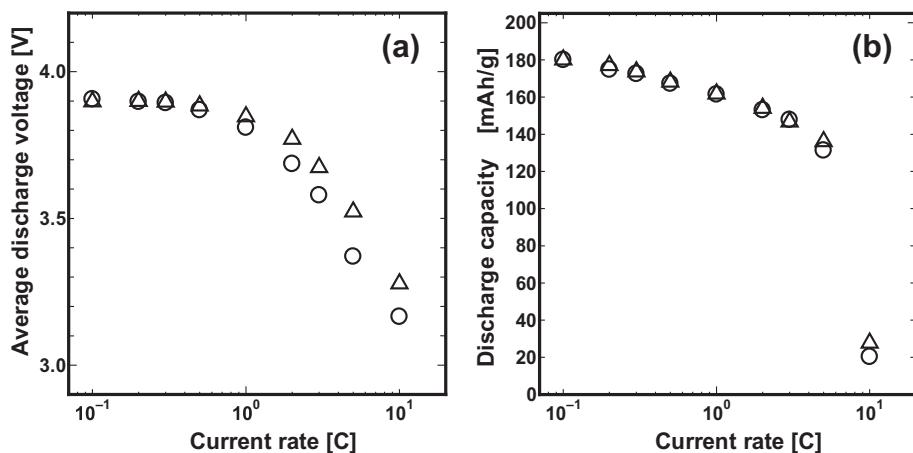


Fig. 5. Variation of the average discharging voltage with discharge current rate (a), and the relationship between the discharge capacity and the discharge current rate (b). Open circles and open triangles denote the values for the cathode prepared on the normal current collector and on the surface-modified current collector, respectively.

on the normal current collector, the charge transfer resistance at the electrode/electrolyte solution interface grew with the electrochemical cycling, while the resistance for the cathode coated onto the surface-modified current collector did not vary with the electrochemical cycling. In general, it is known that the electrode/electrolyte interface resistance increases with the solid/electrolyte

inter-phase formation, due to the degradation of the organic electrolyte solution being in contact with the electrode [12–15]. Following the general previous results, it is likely that the electrode/electrolyte interface resistance depends on SOC state of cathode, surface state of cathode material, chemical compositions of cathode and electrolyte solution and so on. It is unlikely that the

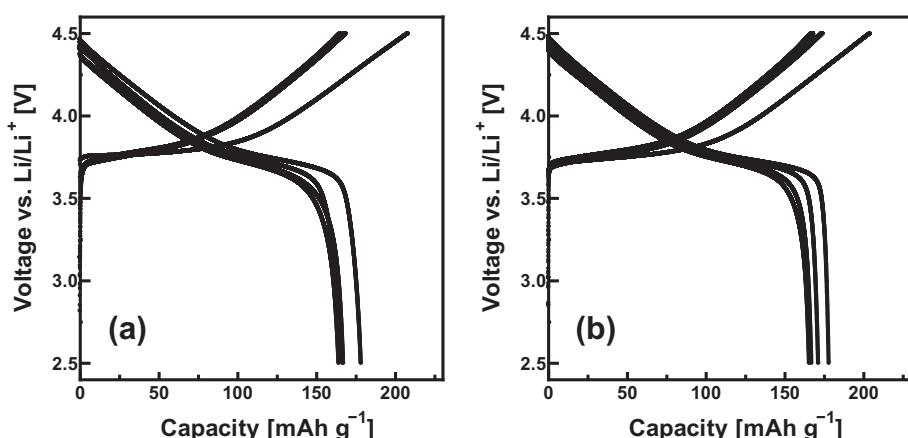


Fig. 6. Charge–discharge profiles of the cathode films prepared on the normal current collector (a) and the surface-modified current collector (b). The curves denote the profiles at 1st, 10th and 20th and 30th cycles at the constant current of 0.1 C.

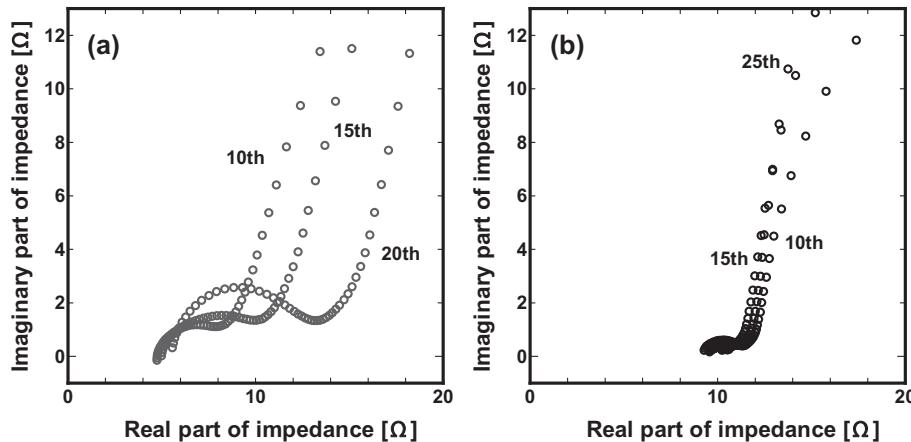


Fig. 7. Nyquist plot of the complex impedance for the cathodes prepared on the normal current collector (a) and on the surface-modified current collector (b). The figures in the viewgraph denote the cycling numbers of the three-electrode cells.

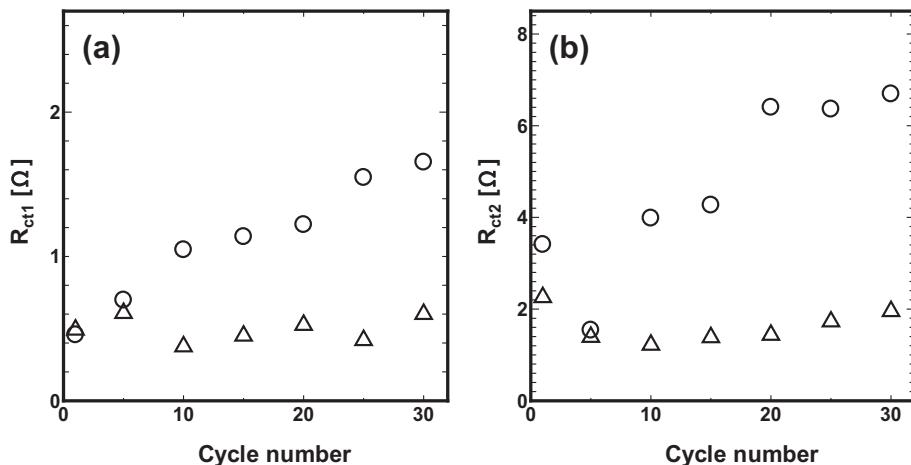


Fig. 8. Variation of the charge transfer resistance with the cycling number: (a) the charge transfer resistance, R_{ct1} , between the current collector and the electrode, and (b) the charge transfer resistance, R_{ct2} , between the electrode and the electrolyte solution. Open circles and open triangles denote the values for the cathode prepared on the normal current collector and on the surface-modified current collector, respectively.

surface morphology of the current collector has an influence on the electrode/electrolyte interface. The reason for the suppression of this interface resistance growth is not clear now, and further detail studies are required.

From these experimental results, it is likely that both the high rate capability and the cycling performance of the cathode prepared on the surface-modified current collector are related to the reduction and stabilization of the charge transfer resistances. In the cathode prepared on the normal current collector, the growth of the charge transfer resistances during the electrochemical cycling can cause poor performances in the high-rate and the cycling characteristics. However, the enhancement of the rate and cycle performances were not as remarkable as expected. This may be attributed to the Ohmic resistance; the Ohmic resistance in the case of using the cathode prepared on the surface-modified current collector was larger than that on the normal current collector, whereas total impedance for the cathode prepared on the surface-modified current collector was surely lower than that on the normal current collector. This increment of the Ohmic resistance is thought to be attributed to the surface oxidation of the Al current collector which comes along with the surface roughening. Hence, the Ohmic resistance may be reduced by the optimization of the surface roughening conditions. If the lowering of the Ohmic resistance is attained, a remarkable improvement of high-rate performance is

expected. More detail studies on the surface treatment should be carried out.

By the way, it was reported that some corrosion of the current collector occurs on the electrochemical cycling and plays an important role for the capacity degradation [16–20]. It is thought that the utilization of the surface-modified current collector may influence the corrosion-related cell degradation. At this problem, the surface-modified current collector has high-resistive oxide surface layer, which can protect the inner part of the current collector from further corrosion. In that situation, an appropriate surface oxide layer gives a positive contribution to the long-term cell performance. Anyway, detail study on the corrosion problem will be one of the important future works.

4. Conclusions

$\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode electrodes prepared onto Al current collectors with different surface morphologies were examined with the electrochemical cycling. Their electrochemical performances, the high-current rate capability and the cycle capacity fading, were sensitive to the surface morphology of the current collector. At the rate capability, the capacity was slightly enlarged and the average discharging voltage was raised using the surface roughened current collector. They have attributed to the polarization, which has

originated as the interface resistances. From the AC complex impedance, it was found that the interface resistance of the cathodes prepared on the surface roughened current collector was always lower than that on the normal current collector. On the other hand, the Ohmic resistance was large in the case of using the current collector with surface roughening. More study on both the increment origin and the optimum surface modification condition will produce more improvement of the battery performance.

Acknowledgment

One of the authors (T.N.) gratefully thanks Dr. M. Tabuchi (National Institute of Advanced Industrial Science and Technology) for their fruitful discussion in addition to their encouragement during this work.

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